

**MICROCAPSULE CONTAINING PHASE-CHANGE MATERIAL  
AND NUCLEATING AGENT**

Related Applications

[0001] This application is a continuation-in-part of Application Serial No. \_\_\_\_\_, filed June 30, 2003, which is a continuation application under 35 U.S.C. § 365 (c) of PCT Application No. PCT/KR01/02151 designating the United States, filed December 12, 2001. The PCT Application was published in English as WO 02/053370 A1 on July 11, 2002, and claims the benefit of the earlier filing date of Korean Patent Application No. 2000/86203, filed December 29, 2000. The contents of the Korean Patent Application No. 2000/86203, the international application No. PCT/KR01/02151 including the publication WO 02/053370 A1, and the prior U.S. application are incorporated herein by reference in their entirety.

Background of the Invention

Field of the Invention

[0002] The present invention relates to a microcapsule containing a phase-change material, to a method of producing the microcapsule, to an article having enhanced heat-retention capability by comprising the microcapsule, and to a method of producing the article.

Discussion of Related Technology

[0003] Dependence on energy imports in Korea is at 97.5 % as they occupy about 20 % of gross domestic imports. Korea is therefore a country with an excessive energy consumption structure. Under the circumstances, since the current price of oil is gradually increasing, there is an urgent need for development of an alternative energy, and to research and develop energy efficiency and energy saving techniques.

[0004] In order to improve the energy efficiency, a heat storage method using a phase-change material is being actively studied at present. The phase-change material is a material capable of absorbing or releasing a significant amount of heat during phase change

versa without temperature variation at a specific temperature. Such heat, which the phase-change material absorbs or releases while maintaining the same temperature during the phase change thereof, is called latent heat. Heat related to the phase change between the solid state and liquid state is called heat of fusion. Heat related to the phase change between the gaseous state and the liquid or solid state is called heat of vaporization. Water is a material in which the phase change between the solid and liquid states occurs at 0°C. When ice melts at 0°C, the latent heat of fusion of ice is 80 cal/gram. That is, when ice is changed to water, the temperature is maintained at 0°C until the heat of 80 cal per 1 gram of the ice is absorbed from the surroundings. There exist numerous materials for which phases are changed at different temperatures.

[0005] Heretofore, studies to improve energy efficiency using latent heat have been centered on inorganic hydrates or molten salts of Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, NaHSO<sub>4</sub>, etc. as the phase-change material. However, there are many difficulties in putting the materials into practical use due to technical limitations such as phase separation, serious subcooling, and bulky volume thereof.

#### Summary of the Invention

[0006] One aspect of the present invention provides a microcapsule comprising a shell and a core enclosed in the shell. The core comprises a phase-change material and a nucleating agent for the phase-change material. The phase-change material comprises a paraffinic hydrocarbon with the melting point of about -30°C or higher, preferably -20°C or higher, more preferably -10°C. The nucleating agent comprises an organic compound miscible with the paraffinic hydrocarbon and having the melting point substantially higher than that of the paraffinic hydrocarbon. The number of carbon atoms in the organic compound is greater than that of the paraffinic hydrocarbon. The paraffinic hydrocarbon has the melting point of about 20°C or higher. The paraffinic hydrocarbon is an unsubstituted paraffinic hydrocarbon. The melting point of the organic compound is higher than that of the paraffinic hydrocarbon advantageously by from about 10°C to about 200°C, preferably by from about 20°C to about 150°C, more preferably by from about 25°C to about 100°C.

[0007] In the above-described microcapsule, the organic compound comprises a

portion that is substantially structurally similar to the paraffinic hydrocarbon of the phase-change material. The paraffinic hydrocarbon is a linear chain hydrocarbon. The organic compound is a substituted linear chain paraffinic hydrocarbon. The paraffinic hydrocarbon and the organic compound are saturated hydrocarbons. The organic compound is a derivative of a paraffinic hydrocarbon. The derivative is a paraffinic hydrocarbon substituted with one or more substituent groups selected from the group consisting of halo; hydroxyl; mercapto; cyano; amine; nitro; carboxyl; formyl; substituted or unsubstituted C1-C20 alkyl; substituted or unsubstituted C2-C10 alkenyl; substituted or unsubstituted C2-C7 alkynyl; substituted or unsubstituted aryl; substituted or unsubstituted heteroaryl; substituted or unsubstituted C3-C7 cycloalkyl, in which a carbon atom in the ring can optionally be replaced by an oxygen, nitrogen or sulfur atom; substituted or unsubstituted C4-C7 cycloalkenyl, in which a carbon atom in the ring can be optionally replaced by an oxygen, nitrogen or sulfur atom; substituted or unsubstituted C1-C20 alkoxy; substituted or unsubstituted C2-C10 alkenyloxy; substituted or unsubstituted C2-C7 alkynyloxy; substituted or unsubstituted aryloxy; substituted or unsubstituted C1-C20 alkylamine; substituted or unsubstituted C2-C10 alkenylamine; substituted or unsubstituted C2-C7 alkynylamine; substituted or unsubstituted arylamine; substituted or unsubstituted alkylarylamine; substituted or unsubstituted C1-C20 alkylsilyl; substituted or unsubstituted C2-C10 alkenylsilyl; substituted or unsubstituted C2-C7 alkynylsilyl; substituted or unsubstituted arylsilyl; substituted or unsubstituted alkylaryl silyl; substituted or unsubstituted C1-C20 alkylboranyl; substituted or unsubstituted C2-C10 alkenylboranyl; substituted or unsubstituted C2-C7 alkynylboranyl; substituted or unsubstituted arylboranyl; substituted or unsubstituted alkylarylboranyl; substituted or unsubstituted C1-C20 alkylthio; substituted or unsubstituted C2-C10 alkenylthio; substituted or unsubstituted C2-C7 alkynylthio; and substituted or unsubstituted arylthio groups. The organic compound is a paraffinic hydrocarbon substituted with one or more substituent groups selected from the group consisting of hydroxyl, amine and carboxyl.

**[0008]** The paraffinic hydrocarbon is a C13-C28 alkane. The organic compound is a C14-C35 alkane substituted with one or more of the above-listed substituent groups. The paraffinic hydrocarbon is selected from the group consisting of n-octacosane, n-heptacosane, n-hexacosane, n-pentacosane, n-tetracosane, n-tricosane, n-docosane, n-heneicosane, n-

eicosane, n-nonadecane, n-octadecane, n-heptadecane, n-hexadecane, n-pentadecane, n-tetradecane and n-tridecane. The organic compound is selected from the group consisting of 1-octacosanol, 1-heptacosanol, 1-hexacosanol, 1-pentacosanol, 1-tetracosanol, 1-tricosanol, 1-docosanol, 1-heneicosanol, 1-eicosanol, 1-nonadecanol, 1-octadecanol, 1-heptadecanol, 1-hexadecanol, 1-pentadecanol, 1-tetradecanol, and 1-tridecanol.

**[0009]** In the above-described microcapsule, the phase-change material may further comprise at least one additional paraffinic hydrocarbon. The number of carbon atoms in the additional paraffinic hydrocarbon is fewer than the number of carbon atoms of the organic compound. The core has a diameter from about 0.1  $\mu\text{m}$  to about 1,000  $\mu\text{m}$ . The diameter may be from about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$ , from about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ , or from about 2  $\mu\text{m}$  to about 10  $\mu\text{m}$ . The nucleating agent is from about 0.1 % to about 15 % with respect to the weight of the phase-change material. The nucleating agent is from about 1 % to about 10 % with respect to the weight of the phase-change material. The nucleating agent is from about 2.5 % to about 7.5 % with respect to the weight of the phase-change material.

**[0010]** The above-described microcapsule has a melting onset temperature (“C” in Figure 2) at which the core begins to melt and a solidifying onset temperature (“D” in Figure 2) at which the core begins to solidify, and wherein the solidifying onset temperature (D) is higher than the melting onset temperature (C). The solidifying onset temperature (D) is higher than the melting onset temperature (C) by a temperature difference from about 0.1°C to about 10°C. The solidifying onset temperature (D) is higher than the melting onset temperature (C) by a temperature difference from about 0.5°C to about 5°C. The shell comprises a polymeric material.

**[0011]** Another aspect of the present invention provides a composition comprising a plurality of the above-described microcapsules. The composition is in a form of powder, liquid or solid having substantial fluidity. The microcapsules are mixed with another material, and wherein the microcapsules form a discrete phase in a continuous phase of the other material. The microcapsules are in an amount from about 0.5 % to about 95 % of the total weight of the composition. The microcapsules may be in an amount from about 5 % to about 90 % of the total weight of the composition. The microcapsules are in an amount

from about 10 % to about 80 % of the total weight of the composition. The composition is in a form of a fabric or a fiber. The composition forms a flooring material. The composition has fluidity to be used as a medium in a cooling or heating system.

**[0012]** Another aspect of the present invention provides a method of using the above-described microcapsule. The method comprises: providing a composition comprising the microcapsule, wherein the composition is powder, liquid or solid having substantial fluidity; mixing the composition with a material for an article with; and forming the article with the mixture. Another method comprises: providing a liquid composition comprising the microcapsule; providing an article of another material; and applying the liquid composition on a surface of the article.

**[0013]** Still another aspect of the present invention provides a microcapsule comprising a shell and a core encapsulated by the shell. The core comprises a phase-change material and a nucleating agent for the phase-change material. The microcapsule has a melting onset temperature (“C” in Figure 2) at which the core begins to melt and a solidifying onset temperature (“D” in Figure 2) at which the core begins to solidify. The solidifying onset temperature (D) is higher than the melting onset temperature (C). The core has a diameter from about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$ . The phase-change material comprises a C13-C28 alkane. The nucleating agent comprises a C13-C35 alkane substituted with one or more substituent groups selected from the group consisting of hydroxyl, amine and carboxyl.

**[0014]** In the above-described microcapsule, the phase-change material comprises an unsubstituted paraffinic hydrocarbon, and the nucleating agent comprises a substituted paraffinic hydrocarbon, in which the number of carbon atoms of the unsubstituted paraffinic hydrocarbon is fewer than that of the substituted paraffinic hydrocarbon. The nucleating agent is from about 0.1 % to about 15 % with respect to the weight of the phase-change material. The solidifying onset temperature (D) is higher than the melting onset temperature (C) by a temperature difference from about 0.5°C to about 5°C. The phase-change material comprises a paraffinic hydrocarbon, and the nucleating agent comprises an organic compound miscible with the paraffinic hydrocarbon and having the melting point substantially higher than that of the paraffinic hydrocarbon, in which the number of carbon atoms in the organic compound is greater than that of the paraffinic hydrocarbon. The

melting point of the organic compound is higher than that of the paraffinic hydrocarbon by from about 10°C to about 200°C. The organic compound comprises a portion that is substantially structurally similar to the paraffinic hydrocarbon of the phase-change material.

[0015] The above-described microcapsule has a melting peak temperature, at which the core is melting with the most latent heat absorption by the core, and a solidifying peak temperature, at which the core is solidifying with the most latent heat release from the core, and wherein a difference between the melting peak temperature and the solidifying peak temperature is not greater than about 20°C. The microcapsule has a melting peak temperature (“E” in Figure 2) and a solidifying peak temperature (“F” in Figure 2.) At the melting peak temperature (E), the core is melting with the most latent heat absorption. At the solidifying peak temperature (F), the core is solidifying with the most latent heat release. A difference between the melting peak temperature (E) and the solidifying peak temperature (F) is not greater than about 20°C. The difference is advantageously not greater than about 15°C, preferably not greater than about 13°C. A difference between the melting onset temperature (C) and the solidifying peak temperature (F) is advantageously not greater than about 10°C, preferably not greater than about 6°C.

[0016] A further aspect of the present invention provides a composition comprising a plurality of the above-described microcapsules. The composition is in a form of powder, liquid or solid having substantial fluidity. A further aspect of the present invention provides a method of using the above-described microcapsule. The method comprises: providing a composition comprising the microcapsule, wherein the composition is powder, liquid or solid having substantial fluidity; mixing the composition with a material for an article with; and forming the article with the mixture. Another method comprises: providing a liquid composition comprising the microcapsule; providing an article of another material; and applying the liquid composition on a surface of the article.

[0017] A still further aspect of the present invention provides a microcapsule comprising a shell and a core enclosed in the shell. The core comprising a phase-change material and means for increasing a solidifying onset temperature beyond a melting onset temperature. Here, the melting onset temperature (“C” in Figure 2) is the temperature at which the core begins to melt, and wherein the solidifying onset temperature (“D” in Figure

2) is the temperature at which the core begins to solidify. The core has a diameter preferably from about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$ , more preferably from about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ . The solidifying onset temperature (D) is higher than the melting onset temperature (C) by a difference preferably from about 0.1°C to about 10°C, more preferably, from about 0.5°C to about 5°C. The microcapsule has a solidifying peak temperature (“F” in Figure 2), at which the core is solidifying with the most latent heat release from the core, and wherein a difference between the melting onset temperature (C) and the solidifying peak temperature (F) is preferably not greater than about 10°C, more preferably not greater than about 6°C.

#### Brief Description of the Drawings

[0018] Figure 1 is a graph showing a subcooled state of a phase-change material contained in a microcapsule.

[0019] Figure 2 is a graph showing that the subcooled phenomenon does not occur when a nucleating agent is added to the phase-change material contained in the microcapsule.

[0020] Figures 3A and 3B illustrate heat flow characteristics of the microcapsules of Example 1.

[0021] Figures 4A and 4B illustrate heat flow characteristics of the microcapsules of Example 2.

[0022] Figures 5A and 5B illustrate heat flow characteristics of the microcapsules of Example 3.

[0023] Figures 6A and 6B illustrate heat flow characteristics of the microcapsules of Comparative Example 1.

[0024] Figures 7A and 7B illustrate heat flow characteristics of the material of Comparative Example 3.

[0025] Figures 8A and 8B illustrate heat flow characteristics of the material of Comparative Example 4.

#### Detailed Description of the Embodiments

[0026] Phase-change materials for use in the embodiments of the present

invention are paraffin hydrocarbons with the number of carbon from 13 to 28. A phase-change material may be selected from a group consisting of n-octacosane, n-heptacosane, n-hexacosane, n-pentacosane, n-tetracosane, n-tricosane, n-docosane, n-heneicosane, n-eicosane, n-nonadecane, n-octadecane, n-heptadecane, n-hexadecane, n-pentadecane, n-tetradecane, n-tridecane and a mixture of two or more of the foregoing, although not limited thereto. A nucleating agent for the phase-change material is to prevent subcooling of the phase-change material.

**[0027]** There have been attempts to efficiently use the latent heat accompanied by the phase change of a material by increasing the surface area of the material through microencapsulation thereof. However, as the conventional microcapsule containing the phase-change material and produced according to the previous attempts is reduced in its size to the order of micrometer, there is a problem in that a serious subcooling of the phase-change material occurs. The subcooling is a phenomenon where a material does not melt when cooled to a temperature below its melting point. The subcooling can be more serious when the diameter of the microcapsules are reduced to the order of micrometer, particularly, 100 micrometers or less. It is known that this is because the droplets of molten liquid are reduced in size and the number of crystallization nuclei in each droplet of molten liquid is simultaneously decreased when the molten liquid is phase-changed to the solid state again. If such subcooling occurs, the latent heat retained by the phase-change material may not be released at an expected temperature.

**[0028]** The present invention is to solve the above problems and is characterized in that the microcapsule containing the phase-change material further contains a nucleating agent together with the phase-change material so that the subcooling of the phase-change material can be prevented and thus the phase-change material can be easily crystallized or solidified at the melting point.

**[0029]** The nucleating agent suitable for preventing the subcooling of the phase-change material may comprise one selected from a group consisting of 1-octacosanol, 1-heptacosanol, 1-hexacosanol, 1-pentacosanol, 1-tetracosanol, 1-tricosanol, 1-docosanol, 1-heneicosanol, 1-eicosanol, 1-nonadecanol, 1-octadecanol, 1-heptadecanol, 1-hexadecanol, 1-pentadecanol, 1-tetradecanol, 1-tridecanol, tridecylamine, tetradecylamine, pentadecylamine,



hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicocylamine, heneicocylamine, dococylamine, tricocylamine, tetracocylamine, pentacocylamine, hexacocylamine, heptacocylamine and octacocylamine. However, the nucleating agent is not limited thereto but may include various other nucleating agents.

[0030] The nucleating material can be added to the phase-change material by the amount of about 0.1 to 15 % with respect to the weight of the phase-change material. However, the amount of the nucleating agent may be varied depending on temperature, and it is preferred that the nucleating agent be used within a range from about 1 to about 10 wt.%.

[0031] The microcapsule according to the present invention can be produced by using a method of coacervation method, an interfacial polymerization method, or an in-situ method, i.e., instantaneously microencapsulating the phase-change material within a reactor. The coacervation method is used, for example, to produce a microcapsule with a wall of gelatin and gum arabic. The interfacial polymerization method uses polyurethane as the wall material of the microcapsule. The in-situ method is used when the phase-change material is microencapsulated in a wall of urea-formaldehyde resin or melamine-formaldehyde resin. Generally, the in-situ method is desirable in that the microcapsule containing the phase-change material can be produced by using the melamine-formaldehyde resin as the wall material, which has superior chemical properties or industrial applicability.

[0032] The in-situ method employed in the present invention will be explained in detail. First, the wall material of the microcapsule is prepared by making a methylol melamine derivative in a process of reacting the melamine and formaldehyde at proper mole fractions under basic conditions. A desired droplet is made by strongly mixing the phase-change material as a core material with an emulsifying agent and by stirring and dispersing them. Subsequently, chemical environment for facilitating a polymerization reaction of the prepared wall material at an interface between the wall material and the core material is created. Then, the wall material is cured to be rigid and dense, and thus, the microcapsule capable of enduring a phase change of the core material is obtained.

[0033] As for the size of the microcapsule of the present invention produced as such, its diameter is within a range of 0.1 to 1,000 micrometers, preferably 0.1 to 300 micrometers. When the phase-change material is produced in the form of the aforementioned

microcapsule having the size of the order of micrometers, a surface area thereof on which heat transfer occurs is increased so that the phase-change material can be efficiently used.

[0034] Proper materials which can be used as the wall material of the microcapsule according to the present invention may include melamine resin, urea resin, gelatin, polyurethane, epoxy, polystyrene, polyvinyl alcohol, and the like. However, they are not limited thereto.

[0035] Meanwhile, firstly, the phase-change material in the microcapsule according to the present invention is enclosed by the polymer matrix wall material of the microcapsule which is densely polymerized. Secondly, upon production of an article comprising the microcapsule, the microcapsule is impregnated into another resin and thus the phase-change material of the microcapsule is enclosed by a second wall of the resin. Accordingly, since the phase-change material in the microcapsule is prevented from leaking out, there is an advantage in that repetitive and reversible use can be made.

[0036] Table 1 below shows the desirable phase-change materials for use in the present invention, the number of carbon atoms thereof, and melting points thereof.

Table 1

Name of materials	Number of carbon atoms	Melting point (°C)
n-octacosane	28	61.4
n-heptacosane	27	59.0
n-hexacosane	26	56.4
n-pentacosane	25	53.7
n-tetracosane	24	50.9
n-tricosane	23	47.6
n-docosane	22	44.4
n-heneicosane	21	40.5
n-eicosane	20	36.8
n-nonadecane	19	32.1
n-octadecane	18	28.2
n-heptadecane	17	22.0

Name of materials	Number of carbon atoms	Melting point (°C)
n-hexadecane	16	18.2
n-pentadecane	15	10.0
n-tetradecane	14	5.9
n-tridecane	13	-5.5

[0037] When each of the phase-change materials is microencapsulated, it has the latent heat of fusion of about 100 J to about 320 J per 1 gram of the phase-change material at the shown relevant melting point thereof. Therefore, the latent heat of the respective phase-change materials can be utilized for enhancing the energy efficiency in proper cases according to their respective melting points.

[0038] For example, one of the phase-change materials which has a melting point of 20°C or higher may be used to be contained in a flooring material. In the case of a flooring material manufactured by impregnating the phase-change material into resin, an aggregate, or the like for constructing the flooring material, when the flooring material is cooled down due to stop of heating thereof after it has been heated so that its temperature is raised up to a certain extent, the phase-change material contained in the microcapsule is solidified again at a predetermined temperature and releases a lot of latent heat. Thus, even though the heating thereof is stopped, the flooring material is maintained at a constant temperature for a long time. It is energy effective in that surplus heat can be utilized. In particular, it is useful to a residence system employing a hypocaust such as a Korean floor heater.

[0039] Among the materials which can be contained in the flooring material, those which have a melting point falling within a range of 20 to 40°C can be used in a state where they are impregnated into a surface layer of a plastic flooring sheet or the like exposed directly to the exterior. The materials which have a melting point of 40°C or higher can be used in a state where they are impregnated into a lower portion of a boiler or the like in which piping is installed or into a concrete base layer around the piping, without exposure to the exterior. In addition, the microcapsule containing such phase-change material may be used in a state where it is impregnated into a thermal insulation material which has been standardized beforehand and manufactured in a type of gypsum board. Alternatively, the microcapsule

containing the phase-change material may be impregnated into proper resin for constructing a flooring sheet as a plastic flooring material so as to produce a standardized plastic flooring material which can be applied in such a manner that it is additionally underlying the existing flooring material.

**[0040]** Meanwhile, such a flooring material may include microcapsules containing two or more different phase-change materials, respectively, to utilize the latent heat accompanied by respective phase changes at different temperatures.

**[0041]** One of the above phase-change materials which has a melting point between 10 to 38°C can be microencapsulated to be used for winter clothes such as skiwear. Furthermore, they can be employed in various other clothes such as fire wear, a diving suit, special working clothes, golf wear, a military uniform, a hat, and gloves; and various articles such as shoes, a carpet, and a blanket.

**[0042]** In addition to the above articles, various articles having enhanced heat-retention capability can be produced by using the microcapsule containing the phase-change material produced according to the present invention. These articles can be easily produced through the known conventional methods by those skilled in the art.

**[0043]** For example, in the case of the flooring material including the microcapsule containing the phase-change material according to the present invention, a flooring material comprising one, two or more layers for constituting a surface layer and a base layer can be produced by impregnating the microcapsule containing the phase-change material according to the present invention into any one or two or more of the layers of the flooring material. At this time, as described above, the flooring material may be the flooring sheet exposed to the exterior, or the additional gypsum board or underlying plastic flooring material installed below the surface layer. Here, the microcapsule may be mixed with and impregnated into other resin forming the surface layer or other components for constituting the gypsum board.

**[0044]** The microcapsule containing the phase-change material according to the present invention may be applied to fabrics including all kinds of fabrics such as woven fabrics, knits, and non-woven fabrics; yarn; and fibers. As also well known to those skilled in the art, a method of applying the microcapsule containing the phase-change material to the

fabrics may include spinning, resin coating, a method of putting a pad comprised of the microcapsules over the fabric, a method of impregnating the microcapsule into the fabric, a method of applying it in the form of a down bag, and textile printing.

**[0045]** Meanwhile, when the microcapsule containing the phase-change material according to the present invention is applied to various articles such as the aforementioned flooring material or fabrics, it is convenient to mix the microcapsule with various kinds of resin according to its use and subsequently to coat or print the articles with the mixture. The resin used for the purpose may include various kinds of UV paints, acryl, polyurethane, silicon, latex, polyethylene, polypropylene, polyvinyl chloride (PVC), epoxy, polystyrene, ethylene/vinyl acetate (EVA) copolymer, rubber, nitrile rubber, polyvinyl alcohol, butyl cellulose acetate, chloroprene rubber, phenol, neoprene, etc. However, the resin employed in the present invention is not limited thereto.

**[0046]** Figure 1 illustrates a pathway of heat flow of microcapsules that do not include a nucleating agent in the core thereof as the temperature changes. As the phase-change material, octadecane was used. Following the arrows drawn on the pathway, the microcapsules in a solid phase are heated and the temperature increases substantially linearly before the point A, which is referred to as “melting onset point”. From the point A, the materials in the core begin to melt, the melting continues over the valley of the pathway. The temperature at the bottom of the valley is where the materials absorb the most of the latent heat during the phase change. After the valley, the temperature of the microcapsules increases substantially linearly as the heat is applied thereto. At about 50°C, heating is stopped, and the microcapsules are cooled. The temperature of the microcapsules decreases substantially linearly as the cooling continues until the point B, which is referred to as “solidifying onset point”. Over the hill of the pathway, the materials in the core of the microcapsules change its phase from liquid to solid and release the latent heat. The top of the hill is the temperature at which the materials release the most of the latent heat during the phase change. After the phase change is complete, the temperature decreases substantially linearly as the microcapsules are cooled.

**[0047]** As illustrated, the melting onset temperature at point A is higher than the solidifying onset temperature at point B. As the microcapsules are cooled, the phase-change

material in the microcapsules does not begin solidifying at a temperature below the point A until it is cooled to the point B. This state of the material at a temperature between point A and point B is called a subcooled state, where the microcapsules do not release latent heat. Further, the temperature of the bottom of the valley at which the most of the heat is absorbed is much higher than the temperature of the top of the hill at which the most of the heat is released.

[0048] Figure 2 illustrates heat flow over temperature of microcapsules of an embodiment of the present invention. A nucleating agent (1-octadecanol) of about 3 % of the weight of the phase-change material (octadecane) was contained in the cores of the microcapsules. Overall, the pathway looks similar to that of Figure 1. The microcapsules in a solid phase are heated and the temperature increases substantially linearly before the point C, which is referred to as “melting onset point”. From the point C, the materials in the core begin to melt, the melting continues over the valley of the pathway. The temperature at the bottom point “E” of the valley is referred to as “melting peak temperature,” at which the materials in the core absorb the most of the latent heat during the phase change. After the phase change is complete, the microcapsules with phase-change material in a liquid phase are cooled and the temperature of the microcapsules decreases substantially linearly until the point D, which is referred to as “solidifying onset point”. Over the hill of the pathway, the materials in the core of the microcapsules change its phase from liquid to solid and release the latent heat. The top point F of the hill is where the materials release the most of the latent heat during the phase change. The temperature at the point F is referred to as “solidifying peak temperature.” After the phase change is complete, the temperature decreases substantially linearly as the microcapsules in a solid phase are cooled.

[0049] It is notable that the melting onset temperature at the point C is slightly lower than the solidifying onset temperature at the point D. The difference between the solidifying onset temperature and the melting onset temperature may vary depending upon the selection of the phase-change material and a matching nucleating agent. In an embodiment, the nucleating agent is selected from organic compounds miscible with the phase-change material and having a portion substantially similar to the structural of the phase-change material. Further, the nucleating agent preferably has a melting point

substantially higher than that of the phase-change material, more preferably by a temperature difference from about 10°C to about 200°C, from about 20°C to about 150°C, or from about 25°C to about 100°C. Further, the nucleating agent is selected from organic compounds having the number of carbon atoms more than that of the phase-change material.

[0050] In other embodiments of the present invention, the difference between the solidifying onset temperature and the melting onset temperature may be greater than what is as shown in FIG 2. Preferably, the temperature difference between the solidifying onset temperature and the melting onset temperature is from about 0.5°C to about 5°C. Further, as the solidifying onset temperature becomes higher than the melting onset temperature, the difference between the solidifying peak temperature at the point F and the melting onset temperature at the point C or melting peak temperature at the point E becomes smaller. With these results, there is no subcooling with ultra-fine microcapsules.

[0051] In view of the features and improvement as discussed, the phase-change material and the nucleating agent are contained in the ultra-fine microcapsule having its size of the order of several micrometers. Thus, it is possible to enhance the heat-retention capability of various articles using the microcapsule. Consequently, in an era of energy shortage, it can be used as alternative energy of which efficiency is remarkably increased.

[0052] Additional features and aspects of the present invention and its embodiments will now be discussed in terms of the examples. The following examples are intended to illustrate various aspects and features of the present invention but not to limit the scope of the present invention.

### Examples

#### Example 1

[0053] 250g of octadecane (having 18 carbon atoms) as a phase change material and 12.5g of eicosanol (alcohol having 20 carbon atoms) as a nucleating agent were dissolved to prepare a core material of microcapsules that comprises the phase change material and the nucleating agent. 75g of 37% aqueous formaldehyde solution, 50g of melamine, and 90g of water were added and heated to 70°C to prepare an initial aqueous polycondensation solution of melamine formaldehyde. The prepared core material was mixed with 550g of 5% aqueous solution of ethylene-anhydrous maleic acid copolymer and emulsified with a homogenizer at

7,000 rpm for about 8 minutes to form droplets of emulsion having an average diameter of 5 micrometers. Subsequently, this emulsified system was mixed with an aqueous solution of melamine formaldehyde and stirred at 70°C for 3 hours, and then, pH thereof was set as 8 to 9 with a 20% aqueous caustic soda solution to prepare a dispersion of thermal energy storing microcapsules. Then, powder of the thermal energy storing microcapsules were prepared using spray drying methods.

[0054] The melting and solidification of the prepared microcapsules were analyzed by using a differential scanning calorimeter (DSC). Figures 3A and 3B show the heat flow characteristics the microcapsules in the melting and solidification, respectively. It was confirmed that the subcooling phenomenon was completely eliminated in the thermal energy storing microcapsules, and rather, the solidifying onset temperature was higher by 2.19°C than the melting onset temperature. This results from the increase of the solidifying onset temperature by using an alcoholic derivative, which has more carbon atoms than those of the phase change material, as a nucleating agent, contrary to a conventional method in which a nucleating agent having the same number of carbon atoms as that of a phase change material was used. This is distinguished from the prior art in which the subcooling phenomenon was not completely eliminated and subcooling of 1 to 2°C was present due to the use of a nucleating agent having the same number of carbon atoms as that of a phase change material.

## Example 2

[0055] In order to prepare a core material of microcapsules that comprises a phase change material and a nucleating agent, 137.5g of tetradecane (having 14 carbon atoms) and 112.5g of tridecane were mixed by weight ratio as the phase change material, and 6.25g of eicosanol (alcohol having 20 carbon atoms) was dissolved as the nucleating agent. 75g of 37% aqueous formaldehyde solution, 50g of melamine, and 90g of water were added and heated to 70°C to prepare an initial aqueous polycondensation solution of melamine formaldehyde. The prepared core material was mixed with 550g of 5% aqueous solution of styrene-anhydrous maleic acid copolymer and emulsified with a homogenizer at 7,000 rpm for about 8 minutes to form droplets of emulsion having an average diameter of 5



micrometers. Subsequently, this emulsified system was mixed with an aqueous solution of melamine formaldehyde and stirred at 70°C for 3 hours, and then, pH thereof was set as 8 to 9 with a 20% aqueous caustic soda solution to prepare a dispersion of thermal energy storing microcapsules. Then, powder of the thermal energy storing microcapsules were prepared using spray drying methods.

**[0056]** The melting and solidification of the prepared microcapsules were analyzed by using a differential scanning calorimeter (DSC). Figures 4A and 4B show the heat flow characteristics the microcapsules in the melting and solidification, respectively. The subcooling phenomenon was also completely eliminated in the microcapsules prepared according to this example due to the higher solidifying onset temperature than the melting onset temperature.

### Example 3

**[0057]** The microcapsules were prepared in the same manner as described in Example 1 except that 250g of octadecane (having 18 carbon atoms) as a phase change material, and 25g of octadecanol (alcohol having 18 carbon atoms) as a nucleating agent were dissolved to prepare a core material of the microcapsules, which comprises the phase change material and the nucleating agent. The subcooling phenomenon was also completely eliminated in the microcapsules prepared according to this example due to the higher solidifying onset temperature than the melting onset temperature. This shows that, in order to increase the solidifying onset temperature, it is necessary to increase the part of the nucleating agent relative to the phase change material in a case where the nucleating agent having the same number of carbon atoms as the phase change material is used. The heat flow characteristics the microcapsules in the melting and solidification are shown in Figures 5A and 5B, respectively.

### Comparative example 1

**[0058]** Microcapsules of a phase change material having an average diameter of 5 micrometers were prepared in the same manner as described in Example 1 by using only 250g of octadecane (having 18 carbon atoms) as the phase change material without using a

nucleating agent for core material of the microcapsules. Subcooling of the microcapsules prepared in this comparative example was assumed because the melting onset temperature was higher than the solidifying onset temperature by 11.97 °C. The heat flow characteristics the microcapsules in the melting and solidification are shown in Figures 6A and 6B, respectively.

#### Comparative example 2

[0059] Microcapsules having an average diameter of 300 micrometers were prepared in the same manner as described in Example 1 by using only 250g of tetradecane (having 14 carbon atoms) as a phase change material without using a nucleating agent for the core material of the microcapsules, and by using gelatin and gum arabic as shell material of microcapsules. The melting and a solidifying were analyzed using a differential scanning calorimeter. Although heat flow diagrams of this example are not available, according to an available record, the solidifying onset temperature was higher than the melting onset temperature the by 3.90°C. Thus, there would not have been subcooling. This is interpreted as the number of crystalline nuclei rapidly decreases in microcapsules having a diameter of 100 micrometers or less, resulting in subcooling, whereas microcapsules having a greater diameter do not exhibit the subcooling.

#### Comparative example 3

[0060] The measurement was carried out for bulk powder of octadecane as it is without encapsulation of the octadecane. Subcooling was not found in the phase change material itself. The heat flow characteristics the material in the melting and solidification are shown in Figures 7A and 7B, respectively.

#### Comparative example 4

[0061] The measurement was carried out for bulk powder of nonadecane as it is without encapsulation of the nonadecane. Subcooling was not found in the phase change material itself. The heat flow characteristics the material in the melting and solidification are shown in Figures 8A and 8B, respectively.

Table 2

Example	Phase Change Material	Nucleating Agent	Type	Average Diameter ( $\mu\text{m}$ )	Melting onset temperature ( $^{\circ}\text{C}$ )	Melting peak temperature ( $^{\circ}\text{C}$ )	Solidify-ing onset temperature ( $^{\circ}\text{C}$ )	Solidify-ing peak temperature ( $^{\circ}\text{C}$ )
Example 1	Octadecane	Eicosanol	Micro-capsule	5	24.60	30.44	26.79	22.25
Example 2	Tetradecane and Tridecane	Eicosanol	Micro-capsule	5	-8.16	-2.44	-5.01	-9.56
Example 3	Octadecane	Octadecanol	Micro-capsule	5	23.68	29.25	25.28	21.94
Comp. Example 1	Octadecane	None	Micro-capsule	5	26.92	30.94	14.95	11.00
Comp. Example 2	Tetradecane	None	Micro-capsule	300				
Comp. Example 3	Octadecane	None	Not in micro-capsule		26.69	31.63	26.77	22.31
Comp. Example 4	Nonadecane	None	Not in micro-capsule		31.29	35.69	30.55	26.81

[0062] The embodiments of the present invention have been described only for the illustrative purposes and do not limit the present invention. It should be understood that those of ordinary skill in the art to which the present invention pertains could make various modifications and changes to the invention without departing from the spirit and scope of the invention defined by the appended claims, and such modifications and changes are included within the present invention.